Mixed Conducting Strontium-Doped Lanthanum-Based Perovskite/Lanthanide-Doped Ceria Composites

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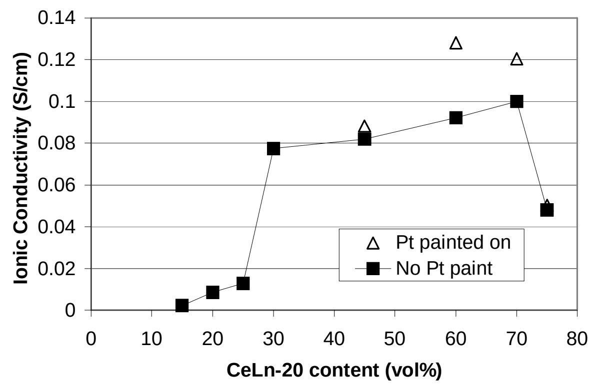
Mixed electron and oxygen ion-conducting materials are potentially useful as selective membranes to separate high-purity oxygen from other gases and for electrodes in solid oxide fuel cells (SOFCs). This work studies a mixed conducting composite consisting of electronically conductive strontium-doped lanthanum chromite, $La_{0.85}Sr_{0.15}CrO_3$ (LSC-15) and ionic conducting lanthanide doped ceria, $Ce_{0.8}Ln_{0.2}O_{1.9}$, (CeLn-20) in which the volumetric ratios of the two phases are varied. Similar studies were also performed replacing LSC-15 with the electronically conductive $La_{0.8}Sr_{0.2}MnO_3$ (LSM-20), and $La_{0.8}Sr_{0.2}FeO_3$ (LSF-20) phases.

Materials were synthesized by glycine-nitrate combustion[1]. Dense samples were prepared by calcination at 1000°C for 1 hour followed by uniaxial pressing at 33 Mpa and isostatic pressing at 130 Mpa. Samples were then sintered to greater than 94% of theoretical density. XRD confirmed that the sintered samples still had the desired phase content. Electrodes were prepared from an ink comprising 50 wt % oxide powder, and 50% screen print binder (Ferro). The ink was screened onto yitria stabilized zirconia and sintered at various temperatures for 2 hrs. The electrodes were characterized using current interrupt cyclic voltametry (CI-CV) and AC impedance.

Micrographs of the sintered samples taken with a scanning electron microscope (SEM) show a random mixture of the two phases which both have an average grain size of 0.5 to 3 μm. The thermal expansion coefficient was found to increase linearly with the volume content of CeLn-20. The isothermal expansion as a function of decreasing pO_2 was also found to increase with CeLn-20 content.

The oxygen ion conductivity was measured by creating an oxygen concentration gradient across the sample, with nitrogen flowing at a controlled rate one on side and pure oxygen flowing on the other side. An oxygen sensor in the nitrogen stream exit was used to quantify the rate of oxygen transport across the cell. The temperature of the sample was cycled between 600° and 1000°C. From these measurements it was found that the percolation threshold of each phase was between 25 and 30 vol%. In the concentration range where both phases were above their percolation thresholds (30 to 70 vol% CeLn-20), the oxygen ion conductivity increased with CeLn-20 content. Painting a



porous Pt layer on both faces of the LSC-15/CeLn-20 composites resulted in an increase in the measured oxygen ion conductivity, suggesting that surface catalysis and/or charge transfer are limiting factors. However, composites in which LSM-20 or LSF-20 is the electronically conducting phase show higher conductivity without the addition of the Pt layer. The total electrical conductivity (electronic and ionic) was measured at 1000°C as a function of oxygen partial pressure (pO_2) between air and 10^{-18} atm using a four-point ac method with Pt electrodes. At constant pO_2, the conductivity decreased with increasing CeLn-20 content. The ionic and total conductivities are further supported by electrochemical measurements.

The composite electrodes were compared to simple single phase electrodes of similar composition without the ceria phase. An interlayer of strontium doped ceria was included in some cases to determine the influence of a continuous barrier layer in preventing formation of the unwanted zirconate resistive layer. As with previous studies on composite electrodes the electrochemical behavior was enhanced by the presence of ceria either as a composite or as an interlayer. The composite was superior to the simple interlayer.

[1] L.A. Chick, L.R. Pederson, G.D. Maupin, J.L. Bates, L.E. Thomas, and G.J. Exarhos, *Mater. Lett.*, 10 (1,2) (1990) 6.